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The use of stepwise differential scanning calorimetry for thermal analysis of foods

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Abstract

Stepwise differential scanning calorimetry was tested for its ability to detect thermal transitions. In this approach, the temperature was increased in 1 K steps, allowing sufficient time between steps for heat flow to reach a steady state. Measurements on ice and indium showed melting to occur within a 1 K step, corresponding with melting points determined by continuous DSC scans. The latent heat of ice melting was linearly correlated with sample weight and used to calibrate the power response. Melting in 20% glucose showed that the end of the melting peak corresponded with the equilibrium freezing point. A phase diagram was developed for sucrose using enthalpy data from a stepwise scan on 20% sucrose, and agreed well with diagrams based on freezing point data. Stepwise scans were also used to study glass transition temperatures in frozen potato and maltodextrin solutions.

Keywords: DSC; Glass transition; Stepwise DSC; Sucrose

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1. Introduction

Differential scanning calorimetry (DSC) has been of tremendous use in monitoring thermal transitions in foods. Phenomena such as the freezing of water, starch gelatinization, or protein denaturation can be studied in this way [1]. DSC operates by measuring the power required to bring the sample cell to a reference cell temperature, while the average temperature of both cells is changed at a programmed rate [2]. The advantage of this approach is that it allows fairly rapid

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determinations of transition temperatures. One drawback is that it does not allow for the finite time required for phase transitions to occur. For example, pure ice would melt at 0°C. However, on a DSC trace, melting continues and latent heat appears to be released at temperatures above 0°C. The peak on the melting curve depends on the sample size; peaks for less massive samples are smaller and appear closer to the true melting point.

There are, of course, routines which correct for this [3]. The onset of a transition may be interpolated from the intersection of a baseline and the rising slope of a transition peak. The end of a transition may be calculated by estimating the thermal lag associated with a sample of a given size. In addition, transition energies can be approximated by the integrated power taken over a larger temperature range.

One way to increase the temperature resolution of a transition is to reduce the scanning rate, see Fig. 3, below. This results in the sample remaining within a given temperature interval for a longer period of time. While this sharpens the peak and gives better discrimination from other transitions, it also reduces sensitivity. This is because the DSC measures heat flow per time. At more rapid scanning rates, the full range of the transition is covered quickly and a greater driving force remains for heat flow. At slower scanning rates, the heat is evolved over a longer time base.

In this study, we propose an alternative means of looking at this problem. In this approach, the DSC is programmed to make a series of small temperature jumps, each followed by an isothermal period. Subsequent temperature steps and holding periods follow, until the whole temperature range of interest is examined. In this way, any thermal events can occur within a small temperature window while allowing time for the heat exchange to reach a steady state. The energy delivered and paid back by the DSC heaters all occurs within this window.

In this paper, we describe experiments in which we tested this "stepwise" DSC for use in food research. There are several areas in which this approach might enhance sensitivity or resolution in the thermal analysis of foods. One of these is in the study of glass transitions in frozen foods. In frozen foods, pure glasses do not form as such. As temperature is decreased, a large portion of the water present is transformed to ice before the freeze-concentration of solutes reaches a critical point, C'_g. Once the corresponding equilibrium temperature T'_g is reached, further lowering of the temperature transforms the remaining liquid into a glass [4]. The amount of material existing as a glass may be small in many frozen foods, thus making it difficult to detect a glass transition. In addition, the transition may be obscured by the large heat produced by the onset of melting.

A second area of interest is in the calculation of the amount of water frozen and unfrozen at a given sub-freezing temperature. For solutions, this could be accomplished by adjusting the solute concentration and measuring equilibrium freezing points. Adiabatic and differential compensated calorimetry have been used to measure unfrozen water in foods [5,6]. Here, we tested whether stepwise scanning calorimetry on a DSC could be used for this purpose.

2. Methods

2.1. DSC programming

A Perkin-Elmer DSC-2 differential scanning calorimeter was used in these studies. The calorimeter head was surrounded by a glove box and purged with dry nitrogen. An Intracool refrigerator provided cooling for sub-ambient work. TADS software was used to collect normal scans on samples.

For stepwise experiments, the DSC was operated in manual mode. The analog calorimetric signal was directed to an analog-to-digital converter on board an IBM XT computer. LabTech Notebook software (Laboratory Technologies, Wilmington, MA) was used to read and display the data. For the experiments described here, the DSC was programmed in 1 K steps. For example, for several experiments the calorimeter was started at 230 K. A 1 K step-jump to 231 K was imposed and accomplished within 1 s. Simultaneously, data collection on the IBM was triggered. Data collection was continued at the new isotherm until a steady-state was reached (Fig. 1). For samples under 10 mg in weight, this typically took less than 3 min. After this period, a new step was imposed to bring the temperature to 232 K. This pattern was repeated until the full temperature range of interest was examined.

For analysis, the area between the heat flow curve and the extrapolated baseline was determined for each temperature interval (Fig. 1). Part of the contribution to the calorimetric signal was due to instrumental transients. To correct for this, data were collected for empty pans over the same temperature range. The area under the empty pan peak was also determined. To obtain the true power development due to the sample, the empty pan peak area was substracted from the sample peak area.

2.2. Experiments

We ran several control experiments to check our results. The first of these was to follow the melting of pure ice at different sample weights. In this, we were looking

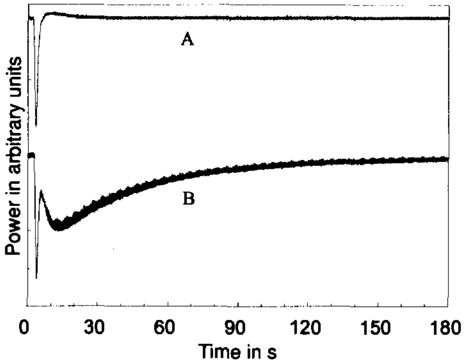

Fig. 1. Power traces developed during stepwise change in temperature (260–261 K): A, empty pan; B, 6.1 mg 20% sucrose.

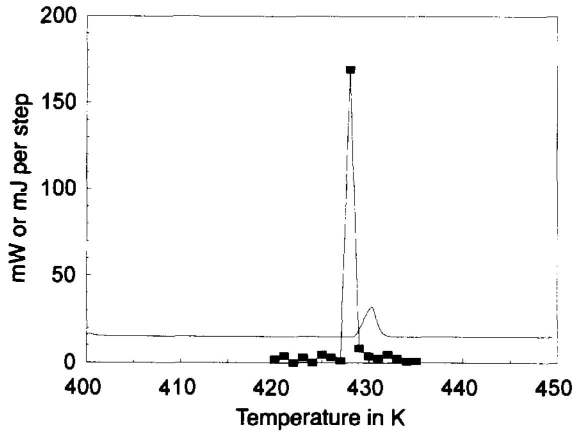

Fig. 2. Continuous (10 K $\min^{-1}$) (——) and stepwise (■) DSC scans for indium melting: continuous scans in mW; stepwise scans in mJ per step.

to see whether the power versus temperature curves were reproducible for a given sample. Secondly, we wanted to see whether the measured transition occurred at the appropriate temperature and produced the requisite latent heat. These results were compared with those obtained by continuous scans on the same sample, and at different heating rates. By using different sample weights we would also see if this had any influence on the measured results. For example, a plot of the latent heat versus sample weight should yield a straight line.

We also scanned samples of indium by both methods (Fig. 2). The onset of melting in the continuous scan occurred at about 428.5 K. In the stepwise scan, all melting occurred within the 428–429 K step. The given melting point of the indium standard was 429.78 K. The heat of fusion for indium was calculated from the stepwise scan using Eq. (2). This gave a value of 29.99 J g^{-1}, compared to the stated value of 28.45 J g^{-1}.

Our first application to food systems was to determine if the glass transition T'_g could be detected, and if so, how its detection compared with that obtained by traditional scanning. We selected dilute maltodextrin (5% M100) and raw potato samples in which we had previously found it difficult to detect T'_g without special sample preparation. The samples were cooled to 220 K, and then scanned continuously or stepwise up to 300 K.

The second set of experiments sought to determine the total amount of heat in frozen sugar solutions, at temperatures between the onset of melting and the initial freezing point. The measured heat was used to calculate the amount of frozen and unfrozen water in the sample at each temperature, using the formula

$$\Delta H = y\Delta H_{\mathrm{lat}} + yC_{p,\mathrm{ice}}(T_{\mathrm{f}} - T) + xC_{p,\mathrm{solids}}(T_{\mathrm{f}} - T) + (1 - x - y)C_{p,\mathrm{H_2O}}(T_{\mathrm{f}} - T) \qquad (1)$$

where T_f is the equilibrium freezing point, x is the weight fraction of solids, y the fraction of ice at temperature $T < T_f$, and $C_{p,\text{ice}}$, C_{p,H_2O}, and $C_{p,\text{solids}}$ are the heat capacities of pure ice, water, and solids, respectively. From these values, phase diagrams were developed and were compared to those developed by other methods.

3. Results

3.1. Response to temperature steps

Fig. 1 shows typical traces resulting from stepwise temperature changes (between 260 and 261 K). The upper curve in Fig. 1 shows heat flow data between an empty sample pan and empty reference pan. The lower curve shows an equivalent situation but with the sample pan containing 6.1 mg of 20% sucrose. For the first 5 s, the samples were at 260 K. At that point, the temperature was stepped to 261 K at a rate of 80 K min^{-1}; the temperature change was accomplished within 1–2 s. At the same time, the power signal changes from its baseline value. As can be seen from the empty pan scan, the maximum excursion occurs 2–3 s after the temperature jump; the power returns to a steady state within 6–10 s. As the empty sample and reference pans are matched, this signal is assumed to be due to instrumental transients associated with the step change.

3.2. Control experiments

Samples of ice were scanned continuously and stepwise from 240 to 298 K (Fig. 3). For the stepwise experiment, the corrected area under the power–time plots was plotted versus temperature. Continuous scans on the same sample were taken at

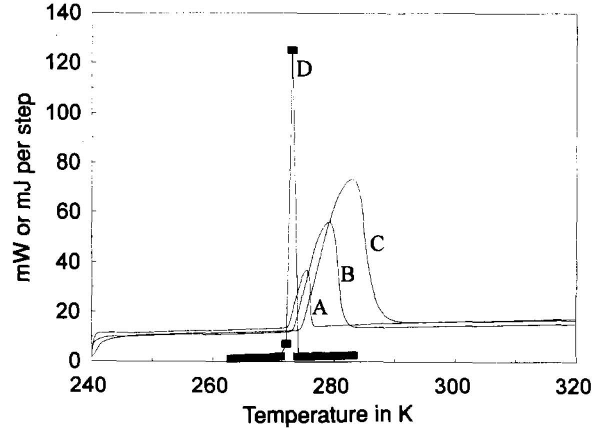

Fig. 3. Continuous and stepwise DSC scans during melting of ice: A, 2.5 K min^{-1}; B, 10 K min^{-1}; C, 20 K min^{-1}; D, stepwise scan: continuous scans in mW; stepwise scans in mJ per step.

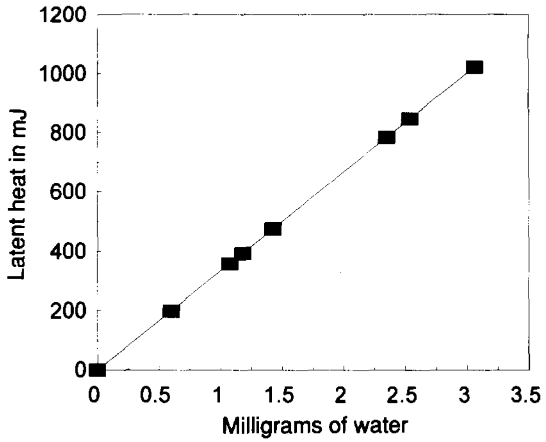

Fig. 4. Latent heat of ice melting determined by stepwise DSC scanning procedure.

2.5, 10, and 20 K min^{-1}. At the slowest scan rate (2.5 K min^{-1}), the melting peak begins at a lower temperature (273 K), is smaller in height, and covers a smaller temperature range (273–278 K). At higher scan rates, the peaks are larger but may begin at a slightly higher temperature; they also cover a larger temperature range (274–291 K for scans at 20 K min^{-1}). In contrast, the stepwise scan shows a very narrow and large peak. Most of the melting occurs within the 273–274 K step.

Stepwise scans were taken of several ice samples of different weights. The calculated heat of fusion is plotted against sample weight in Fig. 4. Linear regression analysis shows high correlation with sample weight ($r = 0.99$). In addition to acting as a check for the performance of the stepwise DSC, these data allowed us to calibrate the absolute heat flow for the system. Thus, for each sample weight m_i, the total heat evolved due to ice melting was just $m_i \times 333.6$ J g^{-1}. Because the signal delivered to the computer is a relative voltage and converted by the A/D converter to a value between +4096 and −4096, these arbitrary units must be converted to a heat flow in standard units. By linear regression, the heat in mJ was related to the heat as measured in A/D units at the computer by

$$\mathrm{Heat}/(\mathrm{J\ g}^{-1}) = 0.817 \times \mathrm{heat}/(\mathrm{A/D\ units}) + 6.97 \qquad (2)$$

DSC scans for 20% glucose are shown in Fig. 5. Here, melting occurs over a broader temperature range. For the continuous scan, the peak appears at 274 K, and the melting curve is completed by 278 K. For the stepwise scan, the melting peak occurs between 269 and 270 K, while melting is completed between 270 and 271 K. The equilibrium freezing temperature for 20% glucose is 270.5 K [7].

3.3. Calculation of phase diagrams

The total enthalpy change between T_f and $T < T_f$ was calculated at several temperatures below T_f for a solution with initial concentration of 20% sucrose.

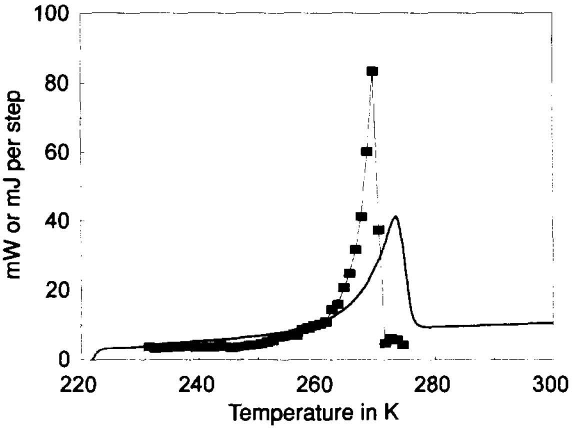

Fig. 5. Continuous (10 K min^{-1}) (——) and stepwise (■) DSC scan during melting of 20% glucose: continuous scans in mW; stepwise scans in mJ per step.

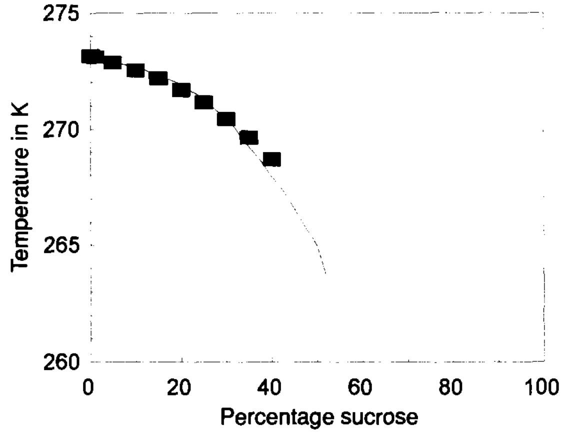

Fig. 6. Phase diagram for sucrose: ■, equilibrium freezing point data [7]; ——, developed from stepwise scan on 20% sucrose solution.

From this, the amount of ice and unfrozen water were determined using Eq. (1). The concentration of sucrose in the unfrozen phase at temperature T is $x/(1-y)$. In this way, an equilibrium phase diagram was developed (Fig. 6). For comparison, curves developed from freezing point depression measurements of solutions of *different* concentrations are also shown. Results from the different approaches are in good agreement.

3.4. Glass transitions

In Fig. 7, continuous and stepwise scans are shown for potato and a 5% maltodextrin solution (M100). For the potato, the continuous scan clearly shows

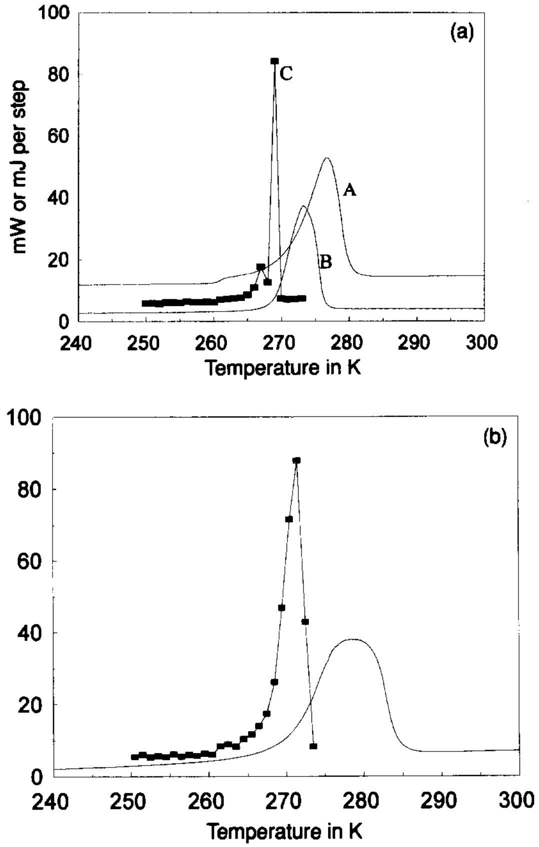

Fig. 7. DSC scans. (a) A, 25% M100; B, 5% M100; and C, 5% M100 (stepwise scan). (b) Potato: ——, continuous scan; ■, stepwise scan. Continuous scans in mW stepwise scans in mJ per step.

ice melting, but does not indicate a clear glass transition. Typically, glass transitions are not seen in the raw potato. They often become apparent if the sample is partially freeze dried or if it is first heated past the starch gelatinization temperature. In the stepped scans, a transition occurs at approximately 260 K in the untreated raw potato. Similarly, continuous scans of 5% M100 do not indicate a clear glass transition; the stepwise scan, however, shows a transition starting at 261 K, peaking at 266 K, and finishing at 267 K. Continuous scans of a more concentrated solution, 25% M100, do show a transition beginning at 260 K.

4. Discussion

The results of these experiments show that the stepwise DSC scans are a reliable alternative for looking at thermal transitions. Control experiments show that the transition temperatures are accurate. Melting of ice, frozen sugar solutions, and indium appear at the appropriate temperatures. Ice and indium melted within a one-step (1 K) interval. The power response was calibrated using the heat of melting of different weights of water. The instrument thus calibrated gave accurate readings for other transition energies, such as indium melting. The one prerequisite was that the instrumental transient response must first be subtracted. This required measurement of an empty-pan power–time plot at each of the temperature intervals under consideration.

The advantage of the stepwise scan is in allowing sufficient time for a transition to occur within a small temperature window. Thus, transitions that are associated with small transition heats may be more easily detected, as that heat is developed within a narrower temperature interval. This may be particularly advantageous if the transition is close in temperature to another one. This was demonstrated in the experiments on glass transitions in maximally freeze-concentrated aqueous systems. Here, the glass transition was obscured by ice melting. This becomes more problematic in systems with higher water concentrations. For example, the glass transition in 25% M100 is easily detected, but is more difficult to detect in 5% M100. However, with the stepwise scan the transition became more apparent, even in the 5% solution. Although we only examined glass transitions in aqueous food systems, stepwise scans should be useful in studying other thermal transitions in food. For example, it may be possible to further resolve the denaturation of the many proteins in meat.

The stepwise scan was also useful in calculations based on partial peak areas. One such case is the determination of the unfrozen water at a given temperature $T < T_f$. This can be measured from the fraction of heat delivered to the sample up to that temperature. In theory, this could be determined from a knowledge of the average heat capacity as a function of temperature. In a continuous DSC scan, the partial heat delivered at a nominal temperature T_i cannot be accurately determined, as the sample is not actually at that temperature. Indeed, the fact that there is an excursion from the baseline indicates that a temperature difference has developed between sample and reference. The DSC x-axis registers average temperature, that is, $T_i = (T_{\text{ref}} + T_{\text{samp}})/2$. The stepwise scan, however, acts as a true heat capacity measurement. All of the heat that is delivered is done so within the temperature increment to which it applies. In the simple case, this was seen in the melting of pure ice. Here, all of the latent heat was absorbed within the 273–274 K interval. A more complex test was in the calculation of phase diagrams for sucrose. Here, the enthalpy difference $H_{T_f} - H_{T_i}$ was used to calculate the fraction of ice and unfrozen liquid. The phase diagram derived in this manner agreed well with that developed from equilibrium freezing point measurements.

There were a few disadvantages to using stepwise scanning. Firstly, the total scanning time is much longer. A 50 K scan took a minimum of 150 min, whereas a continuous scan at 10 K min^{-1} took only 5 min. In addition, much greater time is required to analyze data from the stepwise scan. For a 50 K continuous scan, about 500 data points were collected. For the stepped scan, 1800 points were collected for each 1 K temperature interval, or 90 000 points for a 50 K temperature range. Another consideration is that the resolution of the scan is limited by the size of the steps. For example, in our experiments the melting temperature of ice was determined to within 1 K. This could be improved by taking smaller temperature steps, but at the cost of longer scanning time and, in some cases, reduced sensitivity.

In conclusion, the stepwise scanning procedure was found to be reliable and useful for a few select problems in food science. In our future research, we hope to expand some of the potential applications of this method to other food systems.

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